8. Conclusions

The salient features of the results obtained and their summary are illustrated along with the important conclusions drawn in the present thesis program.

- The CDM activities are carried out in a fixed bed quartz micro-reactor operated in a down flow mode at temperatures of 500-900 °C and ambient pressures.
- The CDM process is influenced by parameters like amount of active metal, nature of support material, reaction temperature, catalyst calcination temperature, mode of reduction, precipitation pH and Ni precursor.
- The catalytic activity is also influenced by the amount of second metal component i.e. Cu, which could enhance methane decomposition activity of the active Ni component at higher temperatures.
- 20 wt% Ni loading is found to be optimum loading over HY zeolite, that posses higher activity than other zeolite systems.
- Ni-Al_2O_3-SiO_2 (4:0.5:1.5) catalyst is reduced with N_2H_4 showed superior activity over all the Ni-based systems at 550 °C reaction temperature.
- It is observed that the addition of Cu to Ni supported systems enhances methane decomposition activity when it is added in an appropriate amount. It is also observed that the Ni-Cu-Al_2O_3 (60:25:15) catalyst pose higher hydrogen yields over other Ni-Cu-Al_2O_3 compositions.
- Decomposition results revealed that the quantity of Cu presence in Ni-Cu-SiO_2 catalysts have significantly influenced methane decomposition activity of Ni. The catalyst Ni-Cu-SiO_2 (60:25:15) calcined at 450 °C for 5 h showed high carbon accumulation of 801 gC/gNi at 650 °C.

- Over all, the hydrogen (or) carbon yields are increasing with the systems in the order of 20 wt% Ni/HY < Ni-Al_2O_3-SiO_2 (4:0.5:1.5) < Ni-Cu-Al_2O_3 (60:25:15) < Ni-Cu-SiO_2 (60:25:15) combinate systems.
- The Ni metal surface areas are calculated from O_2 pulse chemisorption that behaves linear relationship with H_2 yields.
- The XRD patterns of oven dried Ni-Cu-Al_2O_3 and few Ni-Al_2O_3-SiO_2 samples reveal the formation of hydrotalcite like catalyst precursors. However, the HT-like structure is collapsed with the thermal treatment at 450 °C for 5 h in static air.
- XRD spectra of all the fresh samples revealed Ni containing phase is only NiO irrespective of the method of preparation, however, the crystallinity is varied with the preparation method and the amount of Ni. In addition to NiO phase, CuO phase is also observed in few fresh Ni-Cu based samples, where Cu, is present at high loadings.
- All the XRD patterns of deactivated samples have revealed the appearance of metallic Ni phase and is dominated by graphitic carbon phase.
- TPR profiles of impregnated Ni based catalysts showed single reduction center i.e. $Ni^{2+} \rightarrow Ni^0$ (~ 450 °C), in contrast to two reduction centers observed for co-precipitated Ni based catalysts. Also a less intense low temperature peak is observed in between 250-300 °C and is attributed to the reduction of Ni^{2+} species that are not interacted with the support. The second reduction peak is more intense at high temperature peak in the region of 450-700 °C with a T_{max} of 580 °C and is ascribed to the reduction of NiO interacted with the support material presumably due to the formation of amorphous nickel aluminates/silicates.

- The TPR profiles of Ni-Cu based catalysts showed three reduction centers, the low temperature reduction peak (240-260 °C) is due to phase transfer of Cu^{2+} to Cu^0, whereas the moderate temperature reduction peak (425-520 °C) belongs to reduction of Ni^{2+} and is interacted with Cu. The high temperature reduction peak (600-620 °C) is due to the presence of Ni^{2+} interacted with Al_2O_3, SiO_2 supports. Furthermore, the T_{max} of moderate temperature reduction peak is shifted towards low temperature with increase in Cu content. The shift in T_{max} is due to the added Cu that produces spillover hydrogen, which considerably accelerates the nucleation of the Ni metal in these reduction conditions, and enhances the reducibility of Ni. This suggests the role of Cu, which enhances the reducibility of dispersed Ni^{2+} species resulting in the shift of T_{max} towards low temperatures.
- XPS results suggests the presence of Ni^{2+} in all the catalysts, however a shift in the binding energy towards higher side with increase in the amount of Al^{3+} or Si^{4+} amounts are observed.
- The relative surface compositions obtained by XPS analysis has indicated that Ni-Cu-Al_2O_3 (60:25:15) sample is enriched with Ni when compared to other Ni-Cu-Al_2O_3 catalysts, that could be one of the reason to pose higher activity.
- The XPS analysis of Ni-Cu-SiO_2 has indicated the main line of Ni 2*p* at BE of 855 eV that implies a change in the chemical state of NiO $\rightarrow$ $NiSiO_3$.
- SEM and TEM images of deactivated catalysts are revealed that the deposited carbon is filamentous in nature and the Ni has occupied at the tip of the filaments. However, the size and length of the filaments are varied with the catalyst compositions.

- Raman spectra reveals the deposited carbon is filamentous in nature and can be distinguished the presence of ordered (G-band) and defective (D-band) structures of carbon. The high CDM activity over Ni-Cu-Al_2O_3 (60:25:15) catalyst could be possibly due to deposition of high amount of ordered carbon when compared to other Ni-Cu-Al_2O_3 catalysts.
- Methane decomposition results in the decrease of surface area, pore volume, micro-pore volume and increase of average pore diameter revealing that adsorption and decomposition of methane occurs mainly in the micropore of activated carbons.
- The activation energies over activated carbons for methane decomposition are in the range of 170-175 kJ/mol.
- The carbon catalyst COC showed highest initial methane conversion rate of 1.27 mmols/min.g, and a sustainability factor of 0.40 with a carbon yield of 890 mg/g-cat at 900 ºC.

The salient features of all the results obtained in the present thesis work are summarized in Table 8.1.

Table 8.1: Results at a glance on "Study and development of methane decomposition catalysts for CO_X-free hydrogen."

S.No	Catalyst	Weight (mg)	GHSV (L/h. g)	Temp. (°C)	Run time (min)	Carbon yields (gC/g-cat)	Publication
1	20 wt% Ni/HY	50	72	550	850	50	J Power Sources, 164 (2007) 809-814 Catalysis Letters, 118 (2007) 139-145
2	Ni-Al_2O_3-SiO_2 (4:0.5:1.5)	50	72	550	2700	146	J Natural Gas Chemistry, 17 (2008) 113-119 Int J Hydrogen Energy, 33 (2008) 4809-4818
3	Ni-Cu-Al_2O_3 (60:25:15)	20	180	650	900	310	Int J Hydrogen Energy, 33 (2008) 2704-2713
4	**Ni-Cu-SiO_2 (60:25:15)**	**20**	**180**	**650**	**1800**	**480**	Energy Fuels, In press, 2008
5	AC-COC	200	18	900	180	0.89	Catalysis Communications, 9 (2008) 164-169

N. B.:- The total work carried out under this thesis program is published as "Development of methane decomposition catalysts for CO_X free hydrogen" in Catalysis Surveys from Asia 12 (2008) 229-237 (Review)